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A CHEMICAL STUDY OF THE PREPARATION AND STABILITY
OF AQUEOUS METHYL BROMIDE SOLUTIONSBy R. D. Chisholm and L. Koblitsky,
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INTRODUCTION

An aqueous solution of methyl bromide (0.3 percent by volume)²/ has been used to kill the white-fringed beetle and is now authorized³/ for the treatment of various plants shipped out of the quarantined area. Another aqueous solution (0.15 percent by volume) has shown considerable promise⁴/ for control of larvae of the Japanese beetle. Either solution is made by dissolving methyl bromide in twice its volume of ethyl alcohol, adding this mixture to water, and mixing thoroughly. It was observed that during the preparation of the solution there was a considerable loss of gas. It was also suggested that the methyl bromide might be hydrolyzed in the mixture rapidly enough to modify its insecticidal value. A study was made to determine the influence of different methods of preparation and the temperature

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²/ Livingstone, E. M., Easter, S. S., and Swank, G. R. Methyl bromide in aqueous solutions to control Pantomorus leucoloma and Periclyptus. Jour. Econ. Ent. 33: 531-533. 1940.

³/ Administrative instructions--Modifying the restrictions of the white-fringed beetle quarantine by authorizing treatment by Methyl bromide Solution of balled nursery stock of specified thickness. U.S. Dept. Agr., B. E. P. Q. 503 Revised. March 15, 1940.

⁴/ Donohoe, H. C. Unpublished report. May 1940.

of its components at the time of mixing on the composition of the solution. Consideration was also given to the rate at which methyl bromide is hydrolyzed in the solution.

MATERIALS USED

Ethyl alcohol.--The ethyl alcohol used in these experiments was either denatured or 95 to 98 percent pure.

Methyl bromide.--The methyl bromide was of the commercial grade and was supplied in cans, each holding substantially 1 pound. The average net weight in 10 cans was 456.5 grams, with a range from 451.5 to 462.0 grams. Since the average net weight was within 1 percent of 1 pound, these cans were considered to contain a uniform weight of 1 pound of methyl bromide, and no compensation for the differences in net weight was made in these studies.

GENERAL PLAN AND PROCEDURES

General Plan

The general plan followed in these studies consisted of the preparation of the solution in open containers and in closed containers. The components of the solution were mixed at different temperatures, and the solutions were held for extended periods of time in closed containers and also exposed to air in various ways. The total methyl bromide content, as calculated from a bromide determination, and the free bromide ion were determined at intervals.

Procedures

Method of preparation

In one series of experiments the solutions were prepared in open containers on the basis of 1 pound (262 ml.) of methyl bromide, 524 ml. of ethyl alcohol, and 46 gallons (174 liters) of water, which is equivalent to 2.6 mg. of methyl bromide per ml., or 0.15 percent of methyl bromide by volume. In the second series of experiments the solutions were prepared in closed containers, using the same amount of methyl bromide, both with and without alcohol, and in quantities of water ranging from 46 to 70 gallons.

Open containers.--Preliminary experiments were conducted in which the solutions were prepared in open 5-gallon bottles, the necks of which were 1.25 inches in diameter. The required amount (49 grams) of methyl bromide was weighed in a Dreschel high form gas-washing bottle of 125 ml. capacity, the alcohol (57 ml.) was added, and the solution was mixed gently with the stopper in place. The inlet tube of the gas-washing bottle was closed, the outlet tube was connected to a tube extending to the bottom of the bottle containing a little less than 5 gallons of water, and the methyl bromide-alcohol solution was introduced at the bottom of the bottle. The gas-washing

bottle was rinsed with water twice, the volume in the large bottle was made up to 5 gallons, and the mixture was agitated to insure uniformity. The temperatures of the components and of the final mixture were recorded.

Solutions were also made in a 50-gallon drum, the bung of which was 2.25 inches in diameter. A similar procedure was used, except that a quart jar equipped with inlet and outlet tubes was substituted for the gas-washing bottle. The amounts of materials used were 1 pound of methyl bromide, 524 ml. of ethyl alcohol, and 46 gallons of water.

Closed containers.--Solutions were prepared in a drum of approximately 82 gallons' capacity, with the bung in place and sealed by means of a rubber gasket. A 1/8-inch copper tube was soldered vertically into a hole drilled in the bung, and the tube extended to the bottom of the drum. An applicator designed to discharge the methyl bromide from a 1-pound can was attached to the upper end of this tube. Another tube in the bung was provided for a pressure gauge. The volume of water in the drum ranged from 46 to 70 gallons. The method of preparation was as follows: The required amount of water was weighed in the drum, the alcohol added, and the drum closed. A 1-pound can of methyl bromide was inserted in the applicator, and its contents were discharged into the drum. A record was kept of the gauge pressure at intervals.

Method of analysis

The method used to determine the total amount of bromide in the solution was adapted from the method described by Stenger, Shrader, and Beshgetoor.^{5/} This method involves the use of ethanolamine to hydrolyze the methyl bromide, with the subsequent determination of the bromide ion by the Volhard method.^{6/} In preliminary tests, using a 10-ml. sample and 2 ml. of ethanolamine, it was found that about 6 hours was required for complete hydrolysis to take place. When the amount of ethanolamine was increased to 10 ml., hydrolysis was complete in 1 hour. The exact method used follows.

Ten ml. of the solution were pipetted into a glass-stoppered 250-ml. Erlenmeyer flask containing 10 ml. of ethanolamine, and the flask was closed immediately with a stopper previously lubricated with ethanolamine. The flask was shaken at intervals during 1 hour, after which its contents were acidified with concentrated nitric acid. The bromide ion was determined by the Volhard method. One ml. of 0.1 normal silver nitrate is equivalent to 9.50 mg. of methyl bromide.

The amount of bromide ion originally present was determined by acidifying the solution at once with concentrated nitric acid and titrating it.

^{5/} Stenger, V. A., Shrader, S. A., and Beshgetoor, A. W. Analytical methods for methyl bromide. Indus. and Engin. Chem., Anal. Ed., 11: 121-124. 1939.

^{6/} Scott, W. W., and Furman, N. H. Standard methods of chemical analysis. Ed. 5, v. 1, p. 271. D. Van Nostrand Co., Inc., New York. 1939.

EXPERIMENTAL RESULTS

Composition of Solutions Prepared in Open Containers

In a 5-gallon bottle

Methyl bromide solutions were prepared in a 5-gallon bottle with the components of the solution at temperatures ranging from 1° to 25° C. The uniformity of these solutions was established by analysis of samples drawn from both the top and bottom of the bottle. The calculated methyl bromide content was 2.6 mg. per ml. or 0.15 percent by volume. When the components were mixed at 1° C., solid methyl bromide hydrate was formed. This solution was then warmed slowly until the hydrate disappeared, which took place at about 10° C. The average percent of charge recovered immediately after preparation is shown in table 1.

Table 1.—The composition of methyl bromide-ethyl alcohol-water solutions prepared at different temperatures in open 5-gallon bottles, immediately after preparation

<u>Temperature in °C.</u>		<u>Percent of charge recovered</u>
<u>Water</u>	<u>Alcohol</u>	
25	25	57.7
20	20	61.5
10	25	69.2
1	1	96.1

In a 50-gallon drum

Two solutions were also prepared in quantities of 46 gallons in an open 50-gallon drum. In one case the quantity of the water was roughly measured in small units by volume, while in the second case the water was weighed in the drum, the temperature of the water being 26° C. and 25° C., respectively. The amount of methyl bromide recovered was 61.5 percent and 53.8 percent, respectively, of the amount introduced, which indicates that measuring the water accurately is important.

Another solution was prepared under the above conditions except that the amount of methyl bromide in the charge was increased to 2 pounds in 46 gallons of water at a temperature of 22° C. The amount of methyl bromide recovered was 59.6 percent of the amount introduced. Considering the difference in temperature, this percentage recovered was only slightly larger than the percentage recovered when the solution was prepared at the rate of 1 pound of methyl bromide in 46 gallons of water at a temperature of 25° C.; i. e., the weight of methyl bromide per unit of volume recovered from the solution prepared with a 2-pound charge was about double that recovered when a 1-pound charge was used.

These results indicate that in open containers between 40 and 50 percent of the methyl bromide was lost when the solution was prepared at 25° C., which is a temperature that might be encountered under field conditions. The amount of loss was decreased as the temperature of the solution was decreased, until substantially all the methyl bromide was in the solution prepared at 1° C. Since the temperature of solutions prepared in the field cannot be controlled, the composition of the solutions prepared in open containers would vary widely in methyl bromide content.

It was also indicated that the loss from the 1-pound charge was not due to the solution being saturated with methyl bromide but rather to the method of preparation which did not allow sufficient time for the methyl bromide to be dissolved.

Composition of Solutions Prepared in Closed Containers

Solutions were prepared in a drum of 82 gallons' capacity by the method previously described. The temperature of the water ranged from 11.5° to 26° C., and the quantity of water ranged from 46 to 70 gallons. The data gathered in these experiments are shown in table 2.

Table 2.--The composition of methyl bromide-ethyl alcohol-water solutions prepared at different temperatures in a closed drum.

<u>Water</u>		<u>Pressure in pounds</u>		<u>Percent of charge</u> <u>recovered</u>
<u>Volume</u>	<u>Temperature</u>	<u>per square inch</u>		
<u>in gallons</u>	<u>in °C.</u>	<u>Maximum</u>	<u>Minimum</u>	
46	26	6.5	3.0	80.8
60	25	8.5	1.5	90.0
70	25	10.5	1.5	94.1
70	11.5	5.5	1.0	94.1

These data indicate that when the solution is prepared in a closed drum its composition is not dependent on the temperature of the water at the time of preparation. The greatest percentage of recovery was obtained when the drum was nearly full and sufficient time had been allowed for the gas to go into solution, as indicated by the minimum gauge pressure. Considering the amount of methyl bromide in the vapor phase, it is indicated that substantially all the methyl bromide charge was dissolved when the drum contained 70 gallons of solution.

A few experiments in which the solution was similarly prepared, except that it did not contain any alcohol, indicated that under these conditions alcohol at the concentrations used is not an important factor in the solubility of methyl bromide.

Stability of Solution

In order to determine the rate at which methyl bromide is lost from the solution, experiments were conducted in which the solution was held for periods of time under different conditions with respect to temperature and exposure to air.

Two solutions prepared in 5-gallon bottles by the method previously described were kept tightly stoppered and maintained at a temperature ranging from 10° to 12° C. for a period of 48 hours. An average of 2.2 percent of the original bromide content was lost during this period. The average loss of methyl bromide from two solutions similarly prepared and treated, except that the temperature was approximately 25° C., was equal to 5.3 percent of the average original methyl bromide content.

A solution was prepared in a 5-gallon bottle by the same method and kept in the open bottle maintained at a temperature ranging from 10° to 12° C. for a period of 48 hours. During this period 4.3 percent of its methyl bromide content was lost. Two solutions were similarly prepared and treated, except that the temperature was maintained at approximately 25° C. The average loss of methyl bromide during 48 hours was equal to 14.9 percent of the average original methyl bromide content of the solutions.

Forty-six gallons of the solution were prepared in a 50-gallon drum at a temperature of 25° , and allowed to remain in the open with the bung removed. During 48 hours 35.7 percent of the original methyl bromide content of the solution was lost and in 96 hours the loss was 57.1 percent.

The above experiments were on the basis of limited exposure to air. Other experiments were performed in order to determine the loss of methyl bromide from the solution when a relatively large surface was exposed. Six liter beakers (low form) were filled with the solution and held at room temperature (approximately 27° C.). During a period of 48 hours the average amount of methyl bromide lost was equal to 71.0 percent of the average initial content of the solutions and during 72 hours the average loss was 87.5 percent. All the methyl bromide was lost during 2 hours from a thin layer of the solution in a shallow glass dish placed on the ground in the sunlight.

Experiments were conducted to determine the influence of agitation combined with exposure to air on the loss of methyl bromide from the solution. Forty-six gallons of the solution were prepared in an open 50-gallon drum in the usual manner. Six gallons of this stock solution were drawn from the drum by means of a spigot, analyzed, and diluted with an equal volume of water in a small drum. One gallon of this solution was drawn from this drum as above, analyzed, and sprinkled on 1/3 of a square yard of soil, on the center of which was located a shallow glass dish. It was found, on the basis of 1 pound of methyl bromide in 46 gallons of water, that there was a loss of methyl bromide of 46.2 percent during preparation. There was an additional loss of about 7.5 percent during each of the other operations

enumerated above. The solution retained in the glass dish contained only 23.1 percent of its calculated methyl bromide content.

From these experiments it is indicated that the rate of loss of methyl bromide from the solution is dependent not only upon the method of preparation used but also upon the conditions under which it is held after preparation. The extent to which loss of methyl bromide occurs appears to be dependent upon time, temperature, degree of exposure, and agitation after preparation.

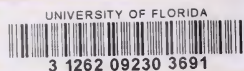
Rate of Hydrolysis of Methyl Bromide

To determine the rate of hydrolysis of methyl bromide in the solution, samples were taken from four solutions at intervals during periods as long as 144 hours after preparation. These samples were titrated immediately on being taken, the same method being used as for the determination of total methyl bromide except that ethanolamine was not used. The average amount of methyl bromide determined was in the order of 0.1 mg. per ml. at each interval. The determination of this quantity of methyl bromide is at about the limit of accuracy of the method of analysis. Since there was no increase in the amount of methyl bromide determined during a period of 144 hours after preparation of the solution, it is indicated that the rate of hydrolysis of this compound under these conditions is not important in relation to its use as an insecticide. Under field conditions, when the solution is applied to soil, the rate of hydrolysis may be modified in the presence of the soil and soil solution. Further studies will be required to determine the behavior of methyl bromide under these variable conditions.

DISCUSSION

It was demonstrated that the methyl bromide content of an aqueous solution of this compound is dependent upon the conditions under which it is prepared and stored. Temperature, exposure to air, and agitation are all variables which modify the methyl bromide content. It was indicated that, since it is difficult to standardize these variables when using an open container, the solution should be prepared in a closed container. Since substantially all the methyl bromide charge is retained in solution when the latter method is used, the use of the closed system would result in a saving of about half of the methyl bromide cost and produce a solution of predetermined methyl bromide content. The closed system referred to is described in detail under "Method of Preparation," which appears in the fore part of this paper.

It is suggested that under field conditions the solution should be prepared by the following method: The container could be a heavy reinforced drum of 100 to 110 gallons capacity. The bung of this drum would be equipped with a pressure gauge and a tube extending to the bottom of the drum and with a strap applicator attached to its upper end. The drum would contain 92 gallons of water. An amount of alcohol equal to twice the volume of methyl bromide may be used if desired. The methyl bromide content of the



solution would be dependent upon the amount of this compound introduced. A charge of 1 pound would produce a solution roughly equivalent to the solution prepared in an open drum containing one-half this amount of water. Precautions should be taken to eliminate leakage of methyl bromide from the applicator and at the points where the tube, pressure gauge, and bung are sealed. Sufficient time should be allowed for the methyl bromide to go into solution, as indicated by the pressure gauge. About 1 hour should be sufficient for the pressure to become less than 1 pound.

Since the methyl bromide content of the solution is dependent on the variables listed above, it is indicated that it should be stored in closed containers to avoid contact with air. In drawing the solution from the drum in which it was prepared, an effort should be made to avoid agitation and exposure as much as possible. It is suggested that a tube be attached to the end of the spigot and extended to the bottom of the container into which the solution is drawn in order to reduce the amount of methyl bromide lost in this operation. After having been drawn from the drum, the solution should be applied to the soil as soon as possible and with a minimum of agitation. It would appear better to pour the solution on the ground rather than to sprinkle it.

SUMMARY

A chemical study was made of the preparation and stability of an aqueous methyl bromide solution used to kill various insects. The composition of the solution prepared in the usual way was found to be dependent upon the temperature of the solution at the time of preparation, which is an uncontrollable variable under field conditions. A loss of between 40 and 50 percent of the methyl bromide charge might be expected when water at a temperature of 25° C. is used. Apparatus was constructed and a method established for the preparation of this solution in a closed container. Solutions prepared in this way retained substantially all the methyl bromide charge. The rate of loss of methyl bromide from the solution was dependent upon time, temperature, degree of exposure to air, and agitation after preparation. The hydrolysis of methyl bromide in the solution during 144 hours was not an important factor. Apparatus and a method for the preparation of the solution in a closed system are described. Suggestions are made for the storage and use of the solution.